GAS PHASE COMBUSTION SUPPRESSION OF VARIOUS FUELS BY CF_3I

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ABSTRACT

This paper presents results of recent studies conducted in our laboratory on the combustion suppression effectiveness of trifluoromethyl iodide (CF_3I) on several gaseous fuels in air. Some interesting results have been obtained that may shed light on the mechanisms of combustion suppression by CF_3I and similar compounds.

To determine some of the effects of the fuel type on the inerting concentration of CF_3I, a set of simple fuels and a gas phase test apparatus were used. A gas flammability apparatus based on ASTM E-681 was used to obtain homogeneous inertion concentrations not dependent on llow rates, position of suppressant injection. or mixing efficiency. The test apparatus used is a 12-liter round glass flask maintained at 60°C. Air and other gases can he fed into the apparatus to measured pressures. A measured amount of water is introduced to give a relative humidity of 50%. A 15 kV. 30 mA power supply connected to a set of platinum electrodes in the flask is used as an ignition source to spark the mixture.

In tests with CF_3I, fuels consisting of a single chemical with small molecules were used to keep complex combustion intermediates to a minimum and to determine whether any trends with regards to chemical stmcture were apparent. **A** mixture of a gaseous fuel and CF_3I was introduced into the apparatus and the mixture sparked. The results, over a range of concentrations, were used to prepare flammability diagrams and to detennine the ratios **of** CF_3I to fuel vapor required for inertion. The results show that the effectiveness of CF_3I varies greatly with the type of fuel used, from effective to highly ineffective. The wide range **of** results was somewhat surprising and may give important clues to the combustion suppression mechanism of CF_3I.

In addition, the gaseous flammability of several pure iodofluorocarbons (IFC) was measured in this apparatus, and, although CF_3I is nonflammable at all concentrations in air, flammability limits were determined under the experimental conditions for perfluoro-n-propyl iodide, perlluoro-n-butyl iodide. and perfluoro-n-hexyl iodide. These are nontlammable liquids by open- and closed-cup, wick, and aerosol spray tests, but. like trichloroethylene and 1,1,1-trichlornethane, they do show flammability limits in air.

INTRODUCTION

Several research groups have conducted extensive and productive studies on the inerting concentrations and combustion chemistry of halons and candidate halon replacements. These groups have included, among others, researchers at NIST, **NMERI,** and the Naval Research Laboratory [1-10].

Since we recognized of the potential attractiveness of CF_3I, other IFCs, and their blends as replacements for ozone-depleting substances we have been investigating the properties and performance of pure IFCs and blends [11-16]. (For some of these publications, see website http://www.etec-nm.com.) Recently **we** have been investigating the flammability of IFC blends. **As** part of these studies, flammability diagrams were prepared for five gaseous fuels with CF_3I in an apparatus based on **ASTM** E-681. The fuels were propane, cyclopropane, isobutane, dimethyl ether, and fluoroethane. **Also** investigated was the behavior in this apparatus of the following three pure low-boiling liquid IFCs under investigation as solvents: perfluoro-n-propyl iodide (1-C_3F_7I), perfluoro-n-butyl iodide (1-C_4F_9I), and perfluoro-n-hexyl iodide (1-$C_6F_{13}I$).

PROCEDURE

A 12-liter round glass flask maintained at 60 °C, as described in ASTM E-681 (revised 1997) were used. The apparatus is shown in Figure 1. Before each test the desired gas mixture for flammability testing was premixed or the pure liquid was placed in *a* syringe. The spark flask was evacuated. The desired pressure of the pure blend or volume of the purc liquid to be tested was introduced (the liquids vaporized immediately). The calculated volume of water to give *50%* relative humidity was injected through **a** septum and vaporized immediately. Dry air was added to bring the flask up to atmospheric pressure. The gas mixture was stirred and allowed to equilibrate at 60 °C. A video camera recorded the test concentrations and the mixture as it was sparked. The spark was controlled to give a current of 30 milliamps at 15,000 volts for 0.4 sec, corresponding to a spark energy of I80 J. If the first spark did not result in *a* positive test, the procedure was repeated twice more. **A** positive Lest was recorded if the tlame reached outside a 45 deg cone extending upward from the spark.

RESULIS

Figures 2 through 6 show the inertion diagrams for the fuels tested with CF_3I. The data were examined in two ways. In the standard approach, the concentration of CF_3I needed to inert any concentration of air in the fuel was determined by drawing a tangent line to the flammable region perpendicular to the CF_3I axis. The ratios of CF_3I to fuel needed to give nonflammable compositions in air were also determined. To achieve this a tangent line was drawn from the origin through the lower borderline of the flammable region. The slope ofthis line gave the minimum ratio of CF_3I to the flammnble component necessary to inert the blend at any concentration in air. This line is referred tu as the dilution line because it represents all possible dilutions of the borderline nonflammable composition in air. Both of these tangent lines are shown for each fuel in Figures 2-6.

Table 1 shows the percentages of CF_3I needed to inert the five fuels tested and the ratios of CF_3I to fuel needed for inertion. All percentages in this paper are given by moles. which for gases is the same as by pressure. The absolute percents of CF_3I needed to inert the fuel have a relatively high uncertainty (±0.5%) because the ratios of extinguishant to fuel were of primary interest.

TABLE I. PERCENTAGES OF CF_3I NEEDED TO INERT THE FIVE FUELS TESTED AND THE RATIOS OF CF_3I TO FUEL NEEDED (BY MOLES).

Flammable Gas	Absolute % CF_3I to Inert Fuel	% CF_3I in Fuel Blend Needed to Inert	Ratio CF_3I/Fuel Needed to Inert
Fluoroethane	4.8	45	0.82
Propane	5.4	57	1.38
Isobutane	5.2	62	I.63
Dimethyl ether	57	>95	>20
Cyclopropane	44	>95	>20

INERTION OF GASEOUS FUELS

Of the fuels tested, fluoroethane (ethyl fluoride) required the lowest percentage of CF_3I to inert (5% absolute or 45% in the fuel blend), followed by propane (6% absolute or 57% in the fuel blend) and isobutane (6% absolute or 62% in the fuel blend). Previous work by NMERI has shown that the CF_3I and Halon 1301 have very similar inerting concentrations for propane in the explosion sphere (6-7% absolute or 54-58% in fuel blends [5,6]). These ratios in fuel blends were calculated from NMERI data by drawing tangent lines from the origin to the explosive regions on published plots of propane vs. agent concentration. Although the NMERI apparatus was somewhat different from ours, the results for propane are in excellent agreement. The results for isobutane are in excellent agreement with the results of an EPA study which found the flammability borderline to be at a ratio of 62% CF_3I to 38% isobutane [17].

CF_3I was found to be extremely ineffective at inerting dimethyl ether or cyclopropane, requiring over 40% absolute or over 95% in the fuel blend. The flammability diagrams revealed that at some concentrations the blends of dimethyl ether or cyclopropane with CF_3I were more flammable in air than the pure fuel.

To explain the somewhat surprising ineffectiveness of CF_3I in inerting dimethyl ether and cyclopropane, the chemical structures and heats of combustion were considered. Chemically, the differences between these fuels and the hydrocarbons or hydrofluorocarbons are that these fuels contain an oxygen atom and a highly strained ring, both of which may significantly effect chemical reactivity. Clearly, these fuels are either increasing the rate of flame radical propagation or heat generated or decreasing inhibitory species. Exothermic chemical reactions may be occurring between CF_3I and dimethyl ether or cyclopropane. However, the data set used is very limited and studies with additional fuels would be needed to determine what is occurring.

The heats of combustion of the fuels [18-20] were examined to determine whether there was a correlation with inerting concentration (Table 2). It is clear that heats of combustion do not explain the inerting concentrations observed. For example, the heat of combustion of dimethyl ether is -348 kcal/mole or –174 kcal/mole per carbon. On this basis alone dimethyl ether would be expected to require similar inertion concentrations to propane or isobutane. Because in fact dimethyl ether was found to be much more difficult to inert than the hydrocarbons, some other important factor is affecting the flammability. Similarly, the heat of combustion of cyclopropane does not help explain the ineffectiveness of CF_3I in inerting it.

As neither thermodynamicists nor combustion chemists, we are aware that the initial calculations and speculations given here are simplistic and imprecise. The data are presented in the hope that interesting results on inerting concentrations will be better interpreted by experts in those areas.

TABLE 2. HEATS OF COMBUSTION OF FUELS.

	-AH,", kcal/mole	$-\Delta H_c^\circ$ per Carbon Atom, kcal/mole
Ethane (for comparison)	373	I86
Propane	530	177
Isobutane	685	171
Cyclopropane	500	I67
Dimethyl ether	348	I74
Fluoroethane	308	154

FLAMMABILITY LIMITS OF LARGER IFCS

ASTM E-681 is a very severe flammability test, much more so than open- and closed-cup, wick, or aerosol spray flammability tests. This is illustrated by the fact that several solvents classified as nonflammable by open- and closed-cup, wick, and aerosol spray flammability tests do have flammability limits in air by ASTM E-681. Trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA, methyl chloroform) are two such examples. We investigated the properties of the three. four, and six-carbon IFCs and found that they also fall into this category. These solvents have no flash point by Tag open and closed cup. Setaflash open and closed cup, and Pensky-Martens closed-cup methods. and are not flammable according to the ASTM wick and aerosol spray tests. Therefore they are classified as nonflammable. However. like TCA and TCE, they have flammability limits in air by ASTM E-681 (Table 3). For comparison, the reported flammability limits for the other halogenated solvents TCA, TCE, and perchloroethylene (PCE) are also listed [21-23]. CFC-113 and PCE have no reported flammability limits in air. It was confirmed by this method that trifluoromethyl iodide has no flammability limits in air.

TABLE 3. FLAMMABILITY LIMITS OF PURE IFCs AND CHLORINATED SOLVENTS IN AIR BASED ON ASTM E-681.

Solvent	Lower Flammability Limit (mole % in air)	Upper Flammability Limit (mole % in air)
CFC-113	None	None
TCA	6.5	15.5
TCE	8	10.5
PCE	None	None
CF_3I	None	None
1-C_3F_7I	13.5	34.5
1-C_4F_9I	8.2	33.1
1-$C_6F_{13}I$	7.5	25.5

The results of this test may be partly explained by the heats of combustion of the IFCs. Simple balancing of the combustion reactions for trifluoromethyl iodide, 1-C_3F_7I, 1-C_4F_9I, 1-$C_6F_{13}I$ gives Reactions 1-4.

$$CF_3I + 2\,H_2O \rightarrow 3\,HF + HI + CO_2 \quad [1]$$
$$1\text{-}C_3F_7I + 4\,H_2O + 2\,O_2 \rightarrow 7\,HF + HI + 3\,CO_2 \quad [2]$$
$$1\text{-}C_4F_9I + 5\,H_2O + 3/2\,O_2 \rightarrow 9\,HF + HI + 4\,CO_2 \quad [3]$$
$$1\text{-}C_6F_{13}I + 7\,H_2O + 5/2\,O_2 \rightarrow 13\,HF + HI + 6\,CO_2 \quad [4]$$

The heats of combustion of the IFCs were calculated from heats of formation. which were calculated from hond dissociation energies for C-C. C-F, and C-I bonds [18-20] and are shown in Table 4. The heats of cornbustion of all IFCs are very low compared to fuel molecules. Still. it is apparent that the heats of combustion of the three, four, and six-carbon IFCs are substantially greater than that of CF_3I on both **a** per-mole and per-carbon-atom basis. This helps explain the fact that they exhibit flammability limits in air, while CF_3I does not.

TABLE 4. CALCULATED HEATS OF COMBUSTION OF IFCs.

	$-\Delta H_c°$, kcal/mole	-AH," per carbon atom, cal/mole
CF_3I	41	41
$1\text{-}C_3F_7I$	206	69
$1\text{-}C_4F_9I$	289	72
	453	76

CONCLUSIONS

Although trifluoromethyl iodide has been shown to be effective in suppressing flammability or explosion of several fuels, it is highly ineffective in suppressing flammability of dimethyl ether or cyclopropane. It is more effective for inerting partially fluorinated hydrocarbons than hydrocarbons. This makes sense in light of the lower heat of combustion and generally easier inertion of partially fluorinated hydrocarbons.

The results show that the effectiveness of CF_3I varies greatly with the type of fuel used. The wide range of results may suggest further studies of combustion chemistry of CF_3I and may give important clues to the suppression mechanism.

The three, four, and six-carbon IFCs tested, although nonflammable by standard solvent flammability tests, have flammability limits in air by ASTM E-681, similar to the nonflammable solvents. TCA and TCE.

ACKNOWLEDGMENTS

We are grateful for support of the work described here by NASA and the US Air Force Research Laboratory.

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